

Density Functional Theory: from theory to Applications

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Recap of previous lecture

Route 2

Car-Parrinello molecular dynamics

Car-Parrinello Lagrangian and equations of motion

Thermostat on the electrons

Analytic and numerical error estimates

CP vs BO

► **Route 2:**

- 1) Maintain the **quantum-mechanical time evolution for the electrons** introducing the separation for the electronic and nuclear wf function in a time-dependent way
- 2) **Time-dependent self consistent field (TDSCF)** approach is obtained.
- 3) **Ehrenfest dynamics** (and as special case Born-Oppenheimer dynamics)
- 4) The classical limit leads then to the **classical molecular dynamics** for the nuclei.

It is possible to follow an alternative route in order to maintain the dynamics of the electron.

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \approx \Psi(\{\mathbf{r}_i\}, t) \chi(\{\mathbf{R}_I\}, t) \exp\left[\frac{i}{\hbar} \int_{t_0}^t \tilde{E}_e(t') dt'\right] \quad (1)$$

where:

$$\tilde{E}_e = \int \Psi^*(\{\mathbf{r}_i\}, t) \chi^*(\{\mathbf{R}_I\}, t) H_e \Psi(\{\mathbf{r}_i\}, t) \chi(\{\mathbf{R}_I\}, t) d\mathbf{r} d\mathbf{R} \quad (2)$$

Inserting this separation ansatz into

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = H \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$$

and multiplying from the left by Ψ^* and by χ^* we obtain

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi \quad (3)$$

$$+ \left\{ \int \chi^*(\{\mathbf{R}_I\}, t) V_n e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) d\mathbf{R} \right\} \Psi \quad (4)$$

$$\hbar \frac{\partial \chi}{\partial t} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi \quad (5)$$

$$+ \left\{ \int \Psi^*(\{\mathbf{r}_i\}, t) H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi(\{\mathbf{r}_i\}, t) d\mathbf{r} \right\} \chi \quad (6)$$

This set of time-dependent Schrodinger equations define the basis of **time-dependent self-consistent field (TDSCF)** method. Both electrons and nuclei moves quantum-mechanically in time-dependent effective potentials.

The classical limit leads to a time-dependent wave equation for the electrons

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \Psi \quad (7)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \quad (8)$$

- ▶ Feedback between the classical and quantum degrees of freedom is incorporated in both direction, even though in a mean field sense.
- ▶ These equations are called Ehrenfest dynamics in honor to Paul Ehrenfest who was the first to address the problem of how Newtonian classical dynamics of point particles can be derived from Schrodinger time-dependent wave equation.

Difference between Ehrenfest dynamics and Born-Oppenheimer molecular dynamics:

- ▶ In ED the electronic subsystem evolves explicitly in time, according to a time-dependent Schrodinger equation
- ▶ In ED transitions between electronic states are possible. This can be showed expressing the electronic wavefunction in a basis of electronic states

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \quad (9)$$

where

$$\sum_{I=0}^{\infty} |c_I(t)|^2 = 1 \quad (10)$$

and one possible choice for the basis functions $\{\Psi_k\}$ is obtained solving the time-independent Schrodinger equation:

$$H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = E_k(\{\mathbf{R}_I\}) \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}). \quad (11)$$

The Ehrenfest dynamics reduces to the Born-Oppenheimer molecular dynamics if only one term is considered in the sum:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$$

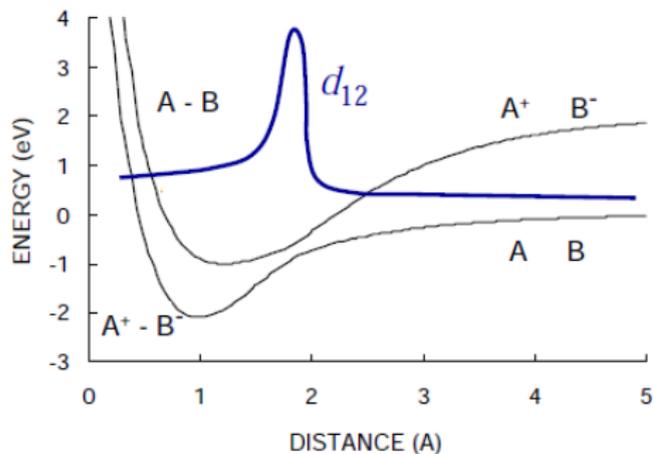
namely:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \Psi_0 \text{ ground state adiabatic wavefunction} \quad (12)$$

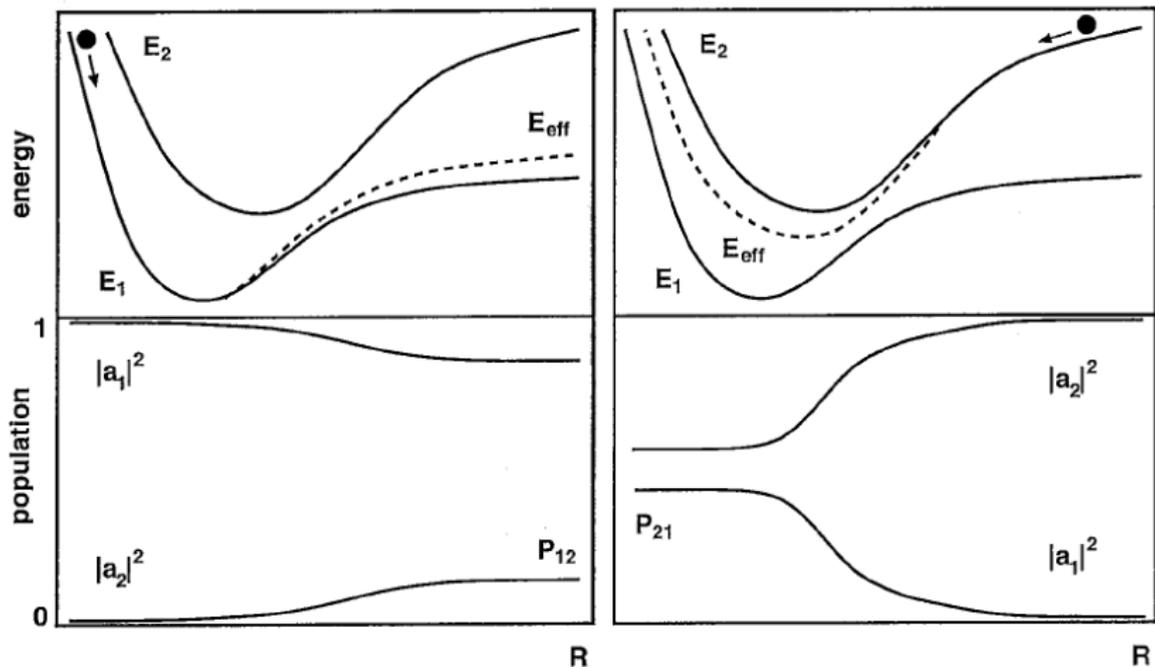
This should be a good approximation if the energy difference between Ψ_0 and the first excited state Ψ_1 is large everywhere compared to the thermal energy scale $K_B T$.

In this approximation the nuclei move on a single adiabatic potential energy surface, $E_0(\{\mathbf{R}_I\})$.

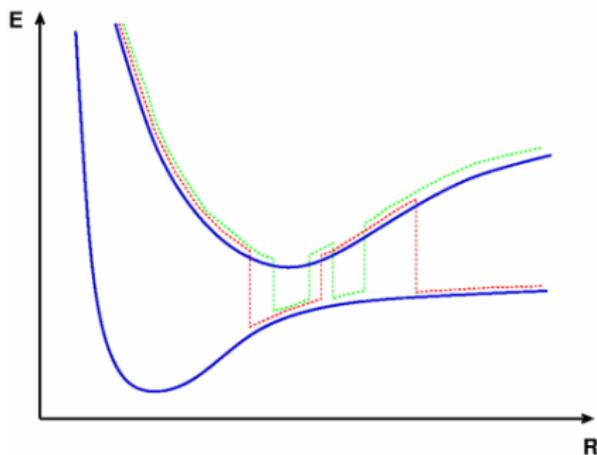
Ionic Molecule (alkali halide)



Nonadiabatic Coupling:
$$d_{12} = \langle \varphi_1 | \partial \varphi_2 / \partial X \rangle$$



Surface hopping



The system is propagated in a pure electronic quantum state, transitions between electronic states are allowed. The probability for a nonadiabatic surface switch depends on the strength of the nonadiabatic coupling. Small gaps generally result in high transition probabilities. Surface hops tend to occur mainly in the vicinity of (avoided) surface crossings.

Classical trajectory calculations on global potential energy surfaces

In BO one can think to fully decouple the task of generating classical nuclear dynamics from the task of computing the quantum potential energy surface.

- ▶ E_0 is computed for many different $\{\mathbf{R}_I\}$
- ▶ data points fitted to analytical function
- ▶ Newton equation of motion solved on the computed surfaces for different initial conditions

Problem: **dimensionality bottleneck**. It has been used for scattering and chemical reactions of small systems in vacuum, but is not doable when nuclear degrees of freedom increase.

Force Field - based molecular dynamics

One possible solution to the dimensionality bottleneck is the force field based MD.

$$V_e^E \approx V_e^{FF} = \sum_{I=1}^N v_1(\mathbf{R}_I) + \sum_{I<J}^N v_2(\mathbf{R}_I, \mathbf{R}_J) + \quad (13)$$

$$\sum_{I<J<K}^N v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \dots \quad (14)$$

The equation of motion for the nuclei are:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{FF}(\{\mathbf{R}_I(t)\}). \quad (15)$$

The electrons follow adiabatically the classical nuclear motion and can be integrated out. The nuclei evolve on a single BO potential energy surface, approximated by a few body interactions.

Ehrenfest molecular dynamics

To avoid the dimensionality bottleneck the coupled equations:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \langle H_e \rangle \quad (16)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \right] \Psi \quad (17)$$

can be solved simultaneously.

The time-dependent Schrodinger equation is solved *on the fly* as the nuclei are propagated using classical mechanics.

Using

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{l=0}^{\infty} c_l(t) \Psi_l(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$$

the Ehrenfest equations reads:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \sum_k |c_k(t)|^2 E_k \quad (18)$$

$$= -\sum_k |c_k(t)|^2 \nabla_I E_k + \sum_{k,l} c_k^* c_l (E_k - E_l) \mathbf{d}_I^{kl} \quad (19)$$

$$i\hbar \dot{c}_k(t) = c_k(t) E_k - i\hbar \sum_l c_l(t) D^{kl} \quad (20)$$

where the non-adiabatic coupling elements are given by

$$D^{kl} = \int \Psi_k^* \frac{\partial}{\partial t} \Psi_l d\mathbf{r} = \sum_I \dot{\mathbf{R}}_I \int \Psi_k^* \nabla_I \Psi_l = \sum_I \dot{\mathbf{R}}_I \mathbf{d}^{kl}. \quad (21)$$

Car-Parrinello molecular dynamics



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Description

Roberto Car with Michele Parrinello, during the Stig Lundqvist Research Conference on the Advancing Frontiers in Condensed Matter Physics, Adriatico Guest House, July 2001

- ▶ Combine the advantages of Ehrenfest and BO dynamics
- ▶ Integrate the equation of motion on a longer time-step than in Ehrenfest, but at the same time
- ▶ take advantage of the smooth time evolution of the dynamically evolving electronic subsystem

Unified Approach for Molecular Dynamics and Density-Functional Theory

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(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

Car-Parrinello method just turned 25!

Car-Parrinello Lagrangian and equations of motion

CP dynamics is based on the adiabatic separation between fast electronic (quantum) and slow (classical) nuclear motion.

They introduced the following Lagrangian

$$\mathcal{L}_{CP} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - \langle \Psi_0 | H_e | \Psi_0 \rangle + \text{constraints} \quad (22)$$

where $\Psi_0 = 1/\sqrt{N!} \det\{\phi_i\}$

and μ is the fictitious mass of the electrons.

the associated Euler-Lagrange equations are:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad (23)$$

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\phi}_i^*} = \frac{\partial \mathcal{L}}{\partial \phi_i^*} \quad (24)$$

from which the Car-Parrinello equations of motion:

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H_e | \Psi_0 \rangle + \frac{\partial}{\partial \mathbf{R}_I} \{constraints\} \quad (25)$$

$$\mu \ddot{\phi}_i(t) = -\frac{\delta}{\delta \phi_i^*} \langle \Psi_0 | H_e | \Psi_0 \rangle + \frac{\delta}{\delta \phi_i^*} \{constraints\} \quad (26)$$

For the specific case of the Kohn-Sham Theory the CP Lagrangian is:

$$\mathcal{L}_{CP} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle + \sum_{i,j} \Lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (27)$$

and the Car-Parrinello equations of motion:

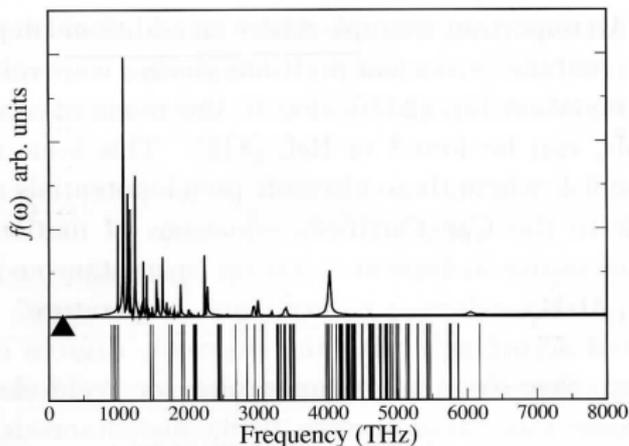
$$M_I \ddot{\mathbf{R}}_I(t) = - \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle \quad (28)$$

$$\mu \ddot{\phi}_i(t) = - H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j \quad (29)$$

The nuclei evolve in time with temperature $\propto \sum_I M_I \dot{\mathbf{R}}_I^2$;
 the electrons have a fictitious temperature $\propto \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle$.

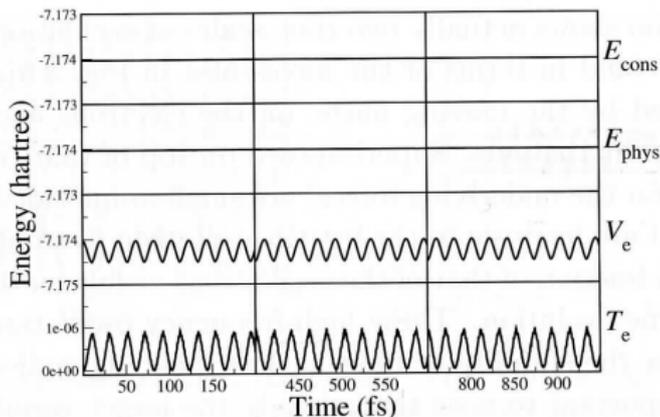
Why does the CP method work?

- ▶ Separate in practice nuclear and ionic motion so that
- ▶ electrons keep cold, remaining close to $\min_{\{\phi_i\}} \langle \Psi_0 | H_e | \Psi_0 \rangle$, namely close to the Born-Oppenheimer surface



$$f(\omega) = \int_0^\infty \cos(\omega t) \sum_i \langle \dot{\phi}_i; t | \dot{\phi}_i; 0 \rangle dt \quad (30)$$

Energy Conservation



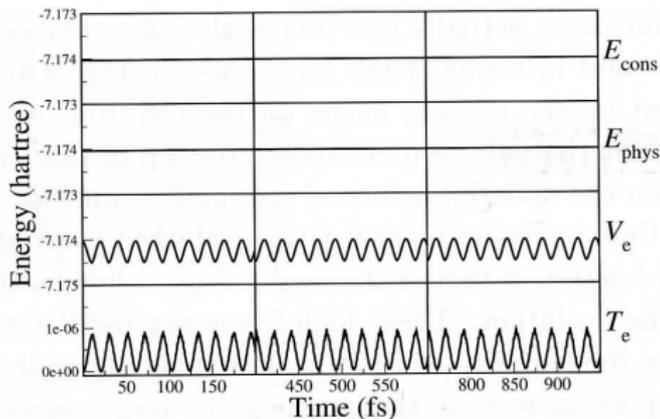
$$E_{cons} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle + \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle \quad (31)$$

$$E_{phys} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle = E_{cons} - T_e \quad (32)$$

$$V_e = \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle \quad (33)$$

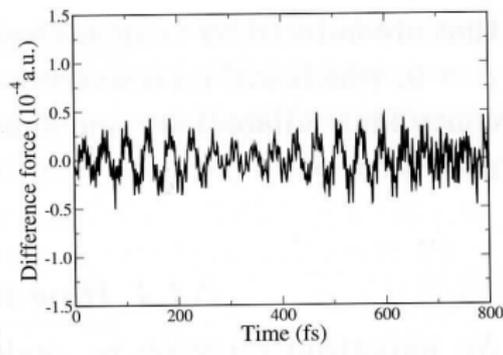
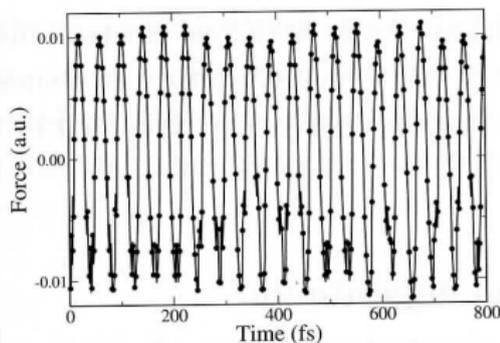
$$T_e = \sum \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle \quad (34)$$

Energy Conservation



- ▶ Electrons do not heat-up, but fluctuate with same frequency as V_e
- ▶ Nuclei drag the electrons
- ▶ E_{phys} is essentially constant

Deviation from Born-Oppenheimer surface



Deviation of forces in CP dynamics from the true BO forces small and/but oscillating.

How to control of adiabaticity?

In a simple harmonic analysis of the frequency spectrum yields

$$\omega_{ij} = \sqrt{\frac{2(\epsilon_i - \epsilon_j)}{\mu}} \quad (35)$$

where ϵ_i and ϵ_j are the eigenvalues of the occupied/unoccupied orbitals of the Kohn-Sham Hamiltonian. The lowest possible electronic frequency is:

$$\omega_e^{min} \propto \sqrt{\frac{E_{gap}}{\mu}}. \quad (36)$$

The highest frequency

$$\omega_e^{max} \propto \sqrt{\frac{E_{cut}}{\mu}}. \quad (37)$$

Thus maximum possible time step

$$\Delta t^{max} \propto \sqrt{\frac{\mu}{E_{cut}}}. \quad (38)$$

In order to guarantee adiabatic separation between electrons and nuclei we should have

- ▶ large $\omega_e^{min} - \omega_n^{max}$.

ω_n^{max} and E_{gap} depend on the physical system, so **the parameter to control adiabaticity is the mass μ** .

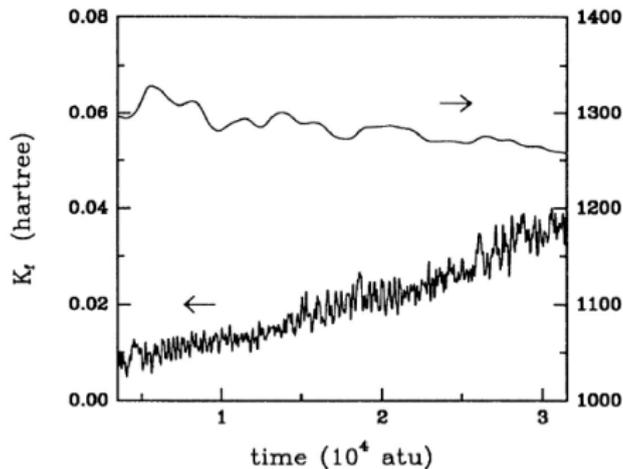
However the mass cannot be reduced arbitrarily otherwise the timestep becomes too small.

Alternatively if Δt is fixed and μ is chosen

- ▶ μ too small: Electrons too light and adiabaticity will be lost
- ▶ μ too large: Time step eventually large and electronic degrees of freedom evolve too fast for the Verlet algorithm

Loss of adiabaticity: the bad cases

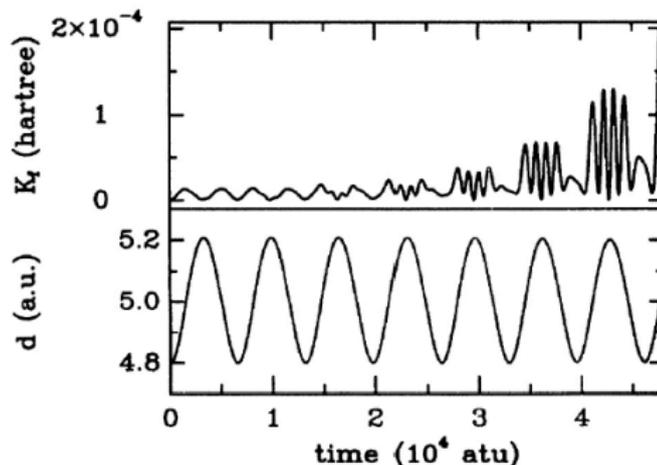
- Vacancy in hot 64-atom Si cell



Due to the presence of the vacancy there is a small gap in the system.

Loss of adiabaticity: the bad cases

- Sn_2 : Degeneracy of HOMO and LUMO at short distances



In this system the gap is periodically opened (up to 0.3 eV) and nearly closed at short distances. The electrons gain kinetic energy in phase with the ionic oscillations.

Zero or small electronic gaps: thermostatted electrons

- ▶ One way to (try to) overcome the problem in coupling of electronic and ionic dynamics is to thermostat also the electrons (Blöchl & Parrinello, PRB 1992)
- ▶ Thus electrons cannot heat up; if they try to, thermostat will adsorb the excess heat
- ▶ Target fictitious kinetic energy $E_{kin,0}$ instead of temperature
- ▶ Mass of thermostat to be selected appropriately:
 - Too light: Adiabacity violated (electrons may heat up)
 - Too heavy: Ions dragged excessively
- ▶ Note: Introducing the thermostat the conserved quantity changes

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle - M_I \dot{\mathbf{R}}_I \dot{\mathbf{X}}_R \quad (39)$$

$$\mu \ddot{\phi}_i(t) = -H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j - \mu \dot{\phi}_i \dot{\mathbf{X}}_e \quad (40)$$

in blue are the frictionous terms governed by the following equations:

$$Q_e \ddot{X}_e = 2 \left[\sum_i \mu \dot{\phi}_i^2 - E_{kin,0} \right] \quad (41)$$

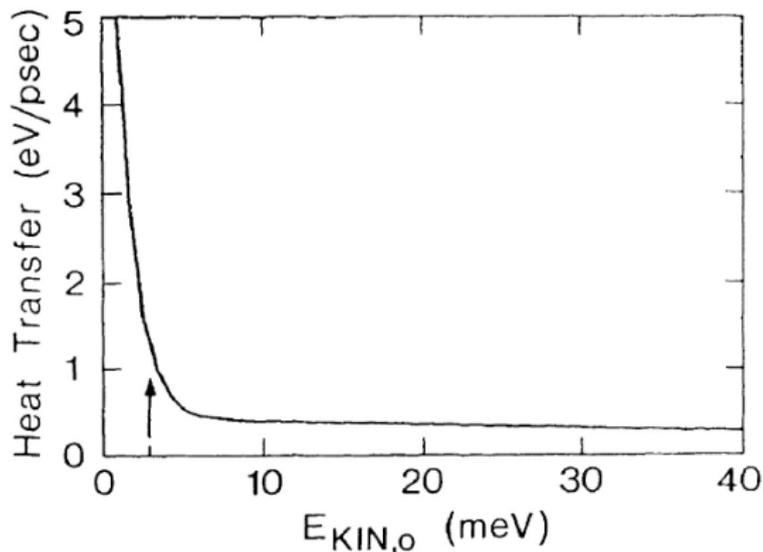
$$Q_R \ddot{X}_R = 2 \left[\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}^2 - \frac{1}{2} g K_B T \right] \quad (42)$$

The masses Q_e and Q_R determines the time scale for the thermal fluctuations. The conserved quantity is now:

$$E_{tot} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle + \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle + \frac{1}{2} Q_e \dot{X}_e^2 + 2E_{kin,0} X_e + \frac{1}{2} Q_R \dot{X}_R^2 + g K_B T X_R \quad (43)$$

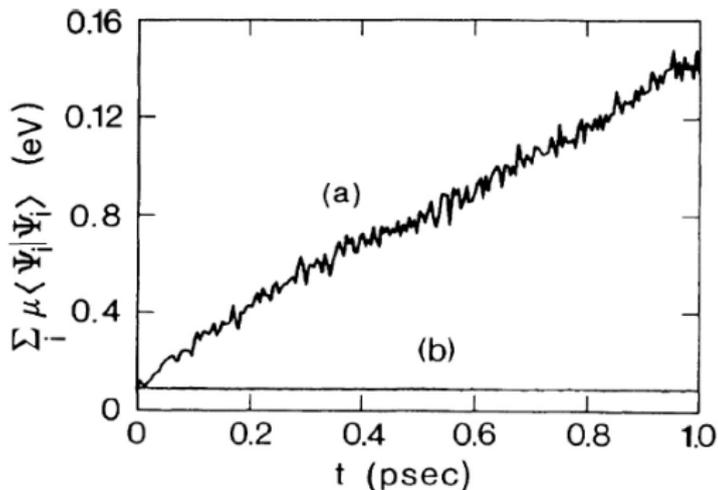
Thermostat on the electrons: examples

- Example: Aluminium
- Dependence of the heat transfer on the choice of $E_{\text{kin},0}$ in solid Al



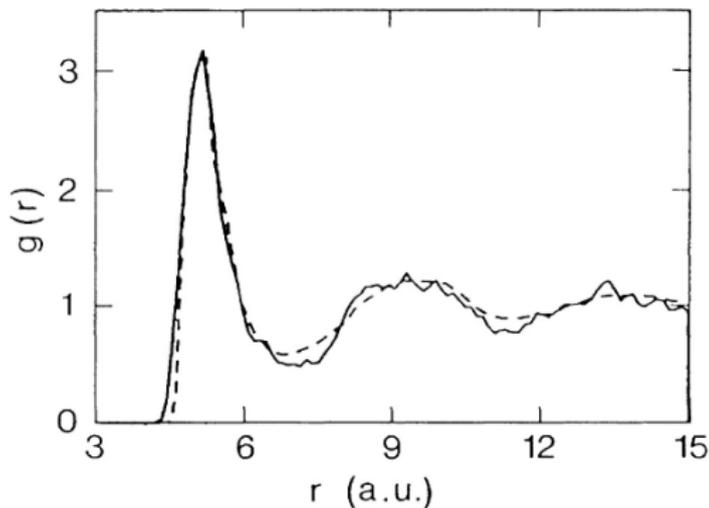
Thermostat on the electrons: examples

- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat



Thermostat on the electrons: examples

- Check: Radial pair correlation function
 - Solid line: CP-MD with thermostat
 - Dashed line: Calculations by Jacucci *et al*



Analytic and numerical error estimates

- ▶ The CP forces necessarily deviate from the BO
- ▶ The primary effect of μ makes the ions "heavier"
- ▶ No effect on the thermodynamical and structural properties, but affect the dynamical quantities in a *systematic* way (vibrational spectra)

$$\phi_i(t) = \phi_i^0(t) + \delta\phi_i(t) \quad (44)$$

Inserting this expression into the CP equations of motions:

$$\mathbf{F}_{I,\alpha}^{CP}(t) = \mathbf{F}_{I,\alpha}^{BO}(t) + \sum_i \mu \left\{ \langle \ddot{\phi}_i | \frac{\partial |\phi_i^0\rangle}{\partial \mathbf{R}_{I,\alpha}} \frac{\partial \langle \phi_i^0|}{\partial \mathbf{R}_{I,\alpha}} | \ddot{\phi}_i \rangle \right\} + \mathcal{O}(\delta\phi_i^2) \quad (45)$$

the additional force is linear in the mass μ so that it vanishes properly as $\mu \rightarrow 0$.

The new equations of motion:

$$(M_I + \Delta_\mu M_I) \ddot{R}_I = F_I \quad (46)$$

where, in the isolated atom approximation,

$$\Delta_\mu M_I = \frac{2}{3} \mu E_{kin}^I = \frac{2}{3} \frac{m_e}{\hbar^2} \sum_j \langle \phi_j^I | -\frac{\hbar^2}{2m_e} \nabla_j^2 | \phi_j^I \rangle > > 0 \quad (47)$$

is an unphysical mass, or drag, due to the fictitious kinetics of the electrons

- ▶ for a system where electrons are strongly localized close to the nuclei there more pronounced renormalization effect

Example: Vibrations in water molecule

mode	harmonic	BOMD	50	100	200	400	dM/M [%]
bend	1548	1543	1539	1535	1529	1514	$0.95 \times 10^{-3} \mu$
sym.	3515	3508	3494	3478	3449	3388	$1.81 \times 10^{-3} \mu$
asym.	3621	3616	3600	3585	3556	3498	$1.71 \times 10^{-3} \mu$

To correct for finite- μ effects:

- ▶ Perform simulation for different μ -values and extrapolate for $\mu \rightarrow 0$.
- ▶ use mass renormalization according to:

$$\omega_{BO} = \omega_{CP} \sqrt{1 + \frac{\Delta_{\mu} M}{M}} \quad (48)$$

Car-Parrinello vs Born-Oppenheimer dynamics

Born-Oppenheimer MD

Exactly on BO surface

$\Delta t \approx$ ionic time scales,
maximum time step possible

Expensive minimisation
at each MD step

Not stable against deviations
from BO surface
 \Rightarrow Energy/temperature drift,
thermostatting of ions necessary

Same machinery in zero-gap systems

Most applications in solids

Car-Parrinello MD

Always slightly off BO surface

$\Delta t \ll$ ionic time scales,
(much) shorter time step necessary

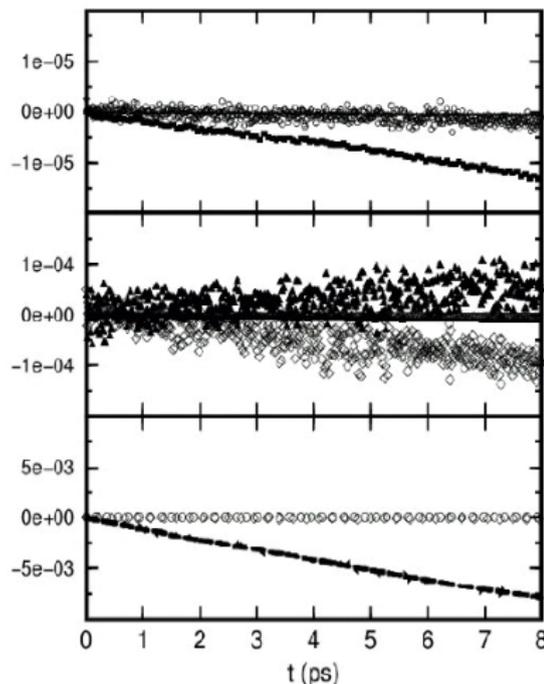
Orthogonalisation only,
less expensive per MD step

Stable against deviations
from BO surface

Thermostatting of electrons
to prevent energy exchange

Superior for liquids

CP vs BO: energy conservation



Δt , convergence

Top:

solid line : CP, 5 a.u.;
open circ. : CP, 10 a.u.;
filled squar. : BO, 10 a.u., 10^{-6} .

Middle:

open circ. : CP, 10 a.u.;
filled squar. : BO, 10 a.u., 10^{-6} ;
filled trian. : BO, 100 a.u., 10^{-6} ;
open diam. : BO, 100 a.u., 10^{-5} .

Bottom:

open circ. : CP, 10 a.u.;
open diam. : BO, 100 a.u., 10^{-5} ;
dashed line : BO, 100 a.u., 10^{-4}

CP vs BO: timing

STABILITY OF BO AND CP MD COMPARED

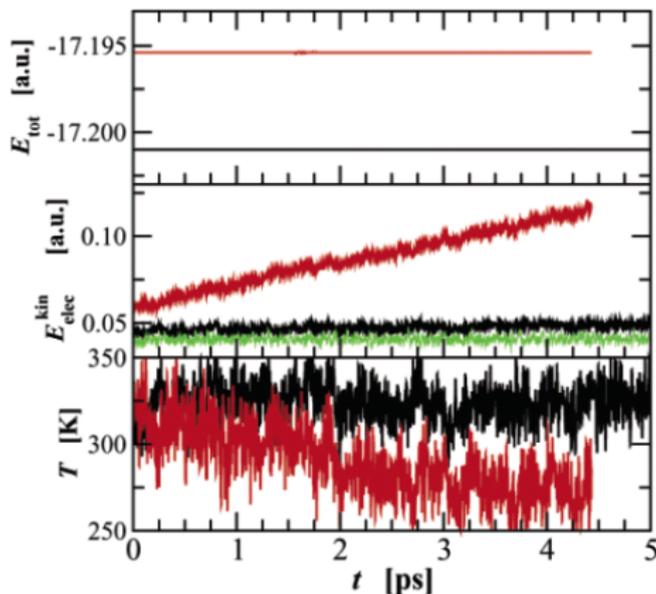
CPMD results for the **8 Si atom model** system

Timings in cpu seconds and energy conservation in a.u. / ps for CP and BO Molecular dynamics simulations for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation

Method	Time step	Convergence	Conservation (au/ps)	Time (s)
CP	5	—	6×10^{-8}	3230
CP	7	—	1×10^{-7}	2310
CP	10	—	3×10^{-7}	1610
BO	10	10^{-6}	1×10^{-6}	16590
BO	50	10^{-6}	1×10^{-6}	4130
BO	100	10^{-6}	6×10^{-6}	2250
BO	100	10^{-5}	1×10^{-5}	1660
BO	100	10^{-4}	1×10^{-3}	1060

Timing in CPU seconds and energy conservation in a.u./ps for

CP of liquid water: Energy conservation



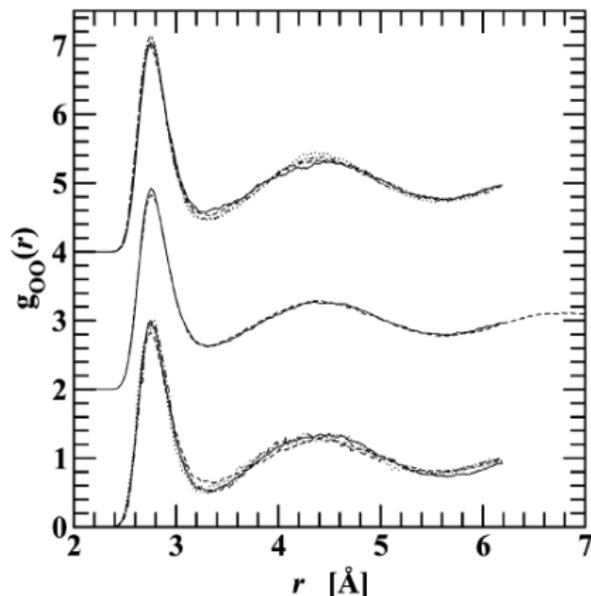
CPMD-800-NVE-64

CPMD-400-NVE-128

CPMD-800-NVT-64

J. Phys. Chem. B 2004, 108, 12990.

CP of liquid water: structure



Oxygen-oxygen radial distribution

BOMD-NVE (solid line)
CPMD-NVE

CPMD-NVE-400-64
CPMD-NVE-400-128

CPMD-NVT-400
CPMD-NVT-800
CP2K-MC-NVT

The radial distribution functions are correct and independent of the method used.

J. Phys. Chem. B 2004, 108, 12990.

Car-Parrinello method: Summary

- ▶ Molecular dynamics can be used to perform real-time dynamics in atomistic systems
- ▶ Verlet algorithm yields stable dynamics (in CPMD implemented algorithm velocity Verlet)
- ▶ Born-Oppenheimer dynamics: Max time step 1 fs (highest ionic frequency $2000-3000 \text{ cm}^{-1}$)
Car-Parrinello dynamics: Max time step 0.1 fs
- ▶ Car-Parrinello method can yield very stable dynamical trajectories, provided the electrons and ions are adiabatically decoupled
- ▶ The method is best suited for e. g. liquids and large molecules with a wide electronic gap
- ▶ The speed of the method is comparable or faster than using Born-Oppenheimer dynamics and still more accurate (i. e. stable)
- ▶ One has to be careful with the choice of $\mu!$